DIFFUSION-CHEMICAL INTERACTIONS IN GLASSES OF THE SYSTEM K₂O – PbO – SiO₂

Yu. A. Guloyan[1]

Diffusion-chemical interactions in glass in the system K₂O – PbO – SiO₂ are analyzed. The interactions are treated from the kinetic standpoint in interrelation with the structural particulars of glasses and the conditions of technological processes.

Key words: diffusion, chemical reactions, lead oxides, rate of processes, adsorption, structural features of glasses.

Lead-containing glasses are widely used in the production of articles for different applications (optical, electro-vacuum, illumination-engineering, dishware, and decorative articles). For this reason, some characteristic of these glasses must be taken into account when organizing technological processes, for example, elevated volatility of lead oxides and the capability of a phase of metallic lead being released under reducing conditions. It should be noted that even though there is a quite substantial number of works in the investigation of the structural properties of lead-containing glasses, specifically glasses of the system K₂O – PbO – SiO₂, there are comparatively few investigations of the technological characteristics of these glasses and the diffusion-chemical interaction in them. This is indicated by, for example, the data of the scientific – technical literature index [1] and the handbook [2]. Some results of investigations in this field and the character of the industrial application of lead-containing glasses are reflected in [3 – 6]. Here, primarily physical aspects of the interaction were studied.

In the present article the diffusion-chemical interactions with volatilization of lead oxides and oxidation-reduction reactions during heat-treatment of glasses in the system K₂O – PbO – SiO₂ are analyzed for compositions of lead crystals used in the production of home glassware (12 – 24% PbO). These interactions are examined from the kinetic standpoint in interrelation with the structural particulars of the glasses and the conditions of commercial technological processes. It is noted that the heterogeneous interaction, specifically, the reduction of lead, includes a stage where nanoparticles form.

VOLATILIZATION OF LEAD OXIDES

Volatilization losses in lead-containing glasses at glass-making and extraction temperatures reach a considerable magnitude, and lead oxides comprise the larger portion of the products of volatilization (up to 90%). This leads not only to the appearance of nonuniformities in molten glass and lower product quality but also to higher consumption of scarce lead-containing materials and environmental contamination.

In [7, 8] mass losses of glass samples per unit surface area were determined in a study of volatilization. Considering the value of the results obtained, it should still be noted that at the present time there are still not enough data to understand the complicated process of volatilization, especially in glass production processes.

The investigations of the character of volatilization of lead oxides were performed on experimental glasses of the system K₂O – PbO – SiO₂ and commercial glasses with PbO content 12 – 24% at temperatures 1200 – 1400°C. The content of lead oxides was determined in thin samples from near-surface layers of glasses made in crucibles, held for a definite period of time in an electric furnace at a prescribed temperature.

Figure 1 shows the kinetic curve of the change in the decrease of PbO at 1350°C. Analysis showed the glass composition to be as follows (%[2]): SiO₂ — 60.1, PbO — 23.9, K₂O — 15.9. As one can see from the figure, the kinetic curve is complicated. The process of volatilization can be analyzed using the kinetic equations for a heterogeneous process [9]. The change of the PbO content as a result of volati-

---

[1] Scientific – Research Institute of Glass, Gus'-Khrustal'nyi, Russia (e-mail: yu_guloyan@mail.ru).
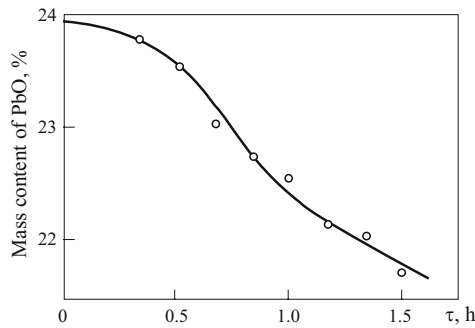
[2] Here and below — content by weight.

Fig. 1. Kinetic curve of the variation of the PbO content in glass.

Fig. 2. Logarithmic anamorphosis of the kinetic curve of the PbO content variation.

Fig. 3. Kinetic parameters versus temperature.

lization proceeds with a decrease of the parameter in time, so that we take as a basis the kinetic equation

$$P_\tau = (P_0 - P_c) \exp(-k\tau^n) + P_0, \qquad (1)$$

where P_τ, P_0, and P_c are, respectively, the instantaneous, initial, and final value of the measured quantity (PbO content); τ is the time; k, n are kinetic parameters of the process.

Comparing Eq. (1) with the equation for the "pure" process of homogeneous kinetics, which is not complicated by parallel processes occurring in the system [10], it is evident that the exponent k characterizes the flow of volume processes in the system. The exponent n of the time, as follows from the derivation of the equation presented in [9], is related with the formation of primary elements of interaction on an interface (in this case, surface sections from which volatilization occurred) and therefore characterizes the flow of surface processes.

In application to volatilization and variation of the PbO content in range 24 – 22%, Eq. (1) has the form:

$$P_\tau = 2\exp(-k\tau^n) + 21.9. \qquad (2)$$

After transformation and taking the logarithm we obtain

$$\log[0.301 - \log(P_\tau - 21.9)] = \log(k \lg e) + n \log \tau. \quad (3)$$

A graphical representation of the logarithmic anamorphosis is presented in Fig. 2. Using the experimental data, we determine the values of the kinetic parameters: n — from the slope angle of the straight line and k — from the initial ordinate. The parameter values are $k = 1.45$ and $n = 2.8$.

Thus the kinetic equation characterizing the variation of the PbO content is

$$P_\tau = 2\exp(-1.45\tau^{2.8}) + 21.9. \qquad (4)$$

As one can see in Fig. 1, the rate of change of the PbO content in near-surface layers of the glass has sections with retarded initial and final stages. Evidently, the main reason for the retardation of the rate at the end of the period considered is volatilization of PbO and K$_2$O from the glass surface and its enrichment by silica. The formation of a surface layer
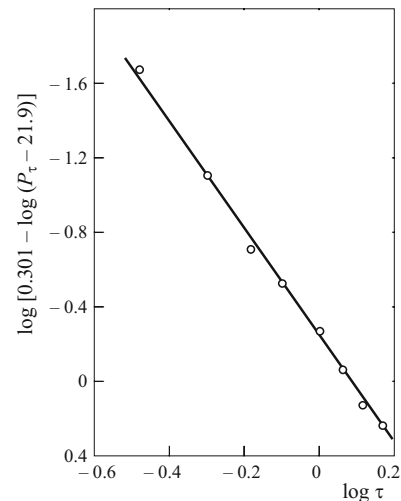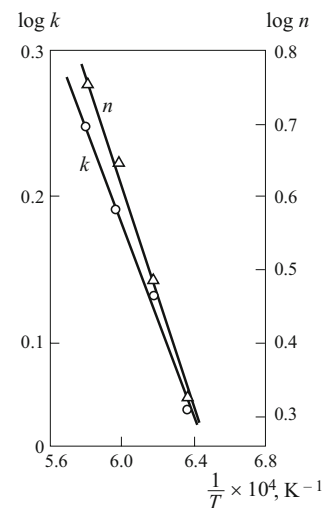
enriched with silica slows the rate of volatilization of the components, particularly, PbO.

The temperature dependence of the kinetic parameters was determined to clarify the effect of temperature on the character of the volatilization. Experiments with different values of the temperature in the range 1300 – 1450°C showed that the temperature dependence of the kinetic parameters follows the Arrhenius exponential equation:

$$k = K \exp\left(-\frac{E_k}{RT}\right); \quad n = N \exp\left(-\frac{E_n}{RT}\right), \qquad (5)$$

where E_k is the activation energy of the volume process, E_n is the activation energy of the surface process, T is the temperature (in K), R is the gas constant, and K and N are constant coefficients.

The temperature dependences are shown in Fig. 3. In accordance with the dependences obtained, the energy parame-
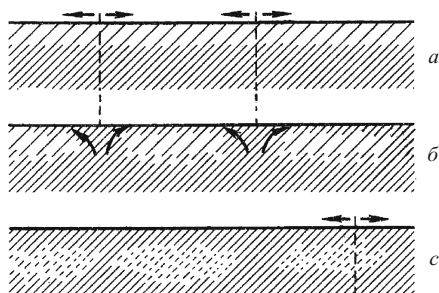
Fig. 4. Scheme of the surface mass transfer accompanying volatilization of the components of glass (PbO): *a*) surface layer enriched with SiO_2 and formation of breaks in it; *b*) lifting of the surface by "fresh" molten glass from lower-lying layers; *c*) spreading of "fresh" molten glass along the surface and displacement of previously formed surface layer into the interior volume of the melt.

ters of the process are $E_n = 74.2$ kJ/mole and $E_k = 127.8$ kJ/mole. The total activation energy of the volatilization process is $E = 202$ kJ/mole. It is evident from Fig. 3 that the kinetic parameter *n*, characterizing the flow of the surface processes, depends more strongly on the temperature than does the parameter *k*. This shows that the temperature has a stronger effect on the process of volatilization from the surface and weaker effect on transfer (diffusion) in the volume of the melt.

Surface phenomena in the glasses of the system K_2O – PbO – SiO_2 play an important role in volatilization of the components from metal, especially PbO. It is known from the data of A. A. Appen, et al. [2] that in the glasses of the present system PbO possesses surface activity. In this connection, positive adsorption of the lead-oxygen groups will occur on the surface. This confirms the assumption that definite structurally shaped lead-oxygen groups, which are weakly bound with the main silicon-oxygen framework, are present glasses [11].

Weak structural binding of lead-oxygen groups in the volume of the glass and especially on the glass surface facilitates the volatilization process. Here it should be noted that the state of the lead-oxygen groups in the surface layer is different from their in the interior volume. In the surface layer the coordination number of lead with respect to oxygen decreases and under the influence of the surface force field the bonds with oxygen become weaker. All this facilitates the volatilization process. Because of these factors, dissociation of lead-oxygen groups can likewise occur in the surface layers: $PbO \rightarrow Pb + O^-$. Volatilization of atomic lead formed as a result of dissociation in the surface layer is facilitated by high vapor pressure (0.25 kPa at 1027°C).

Dissociation in the surface layer is observed for a number of substances even with much stronger bonds than in lead-oxygen groups [11 – 14].

Investigations of the process of volatilization as a function of the PbO content in glass show that the losses accom-

panying volatilization increase with increasing PbO content, especially above 18%.

As noted, the volatilization of the components from the surface results in the enrichment of the surface layer with silica, the appearance of glass with a new composition with much higher viscosity and surface tension. Surface mass transfer occurs; this process is studied by H. Jebsen-Marvedel and R. Brükner [5].

The micro-nonuniformity of the surface and the effect of the surface forces result in the formation of breaks through which "fresh" molten glass flows to the surface from the lower-lying layers with lower surface tension and viscosity. Under the action of surface forces this fresh molten glass spreads along the previously formed surface layer, which is thus displaced into the interior volume of the melt. Volatile components (PbO) are once again removed from the newly formed surface layer and the process repeats. The surface layers enriched with silica and displaced into the volume of the melt serve as a source of formation of striae, which is confirmed by the experimental data. Surface mass transfer is illustrated schematically in Fig. 4.

When industrial technological processes are conducted, especially in making lead crystal and in manual extraction of the articles, the appearance of striae in the articles during the initial period of extraction is mainly due to the this phenomenon. For this reason, when making lead crystal in a crucible furnace it is recommended that the surface layer of the glass be removed before extraction of the articles starts. For glass-making in tank furnaces continuous mixing of the molten glass in the extraction part gives a definite homogenization of the molten glass but results in elevated volatilization of PbO and some decrease of light transmission and index of refraction as a result of the high concentration of fine striae. To decrease volatilization losses and when the productivity is relatively low deep electro-melting under the mix layer should be used. For mechanical extraction of articles made of crystal, in order to eliminate any consequences of PbO volatilization from the surface, feeders with a closed surface of the molten glass are used and stream-apportioned molten glass is fed through the electrically heated platinum tube. The highest requirements for chemical and optical uniformity are applied to optical glasses. In this connection conditions which prevent the appearance of nonuniformities and striae are created: the use of continuous mixing during glass-making, prolonged cooling with mixing, pouring glass off the bottom part, and so forth.

GAS-PLASMA HEAT-TREATMENT

In the heat gas-plasma treatment of glasses in the system K_2O – PbO – SiO_2 diffusion of gases in glass, chemical interaction of gases with the structural elements of the glass, precipitation of a new phase, and interaction of the latter with the surrounding glassy matrix all occur together.
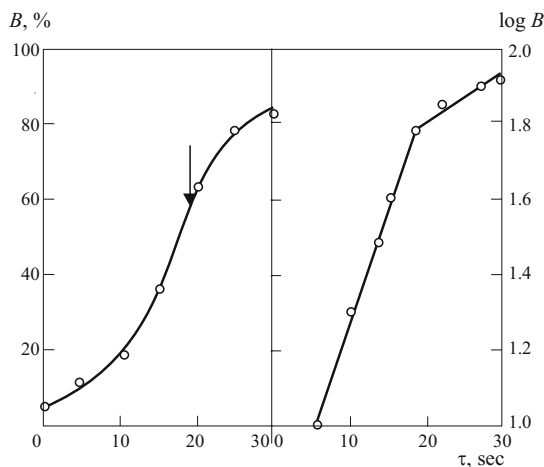
Fig. 5. Kinetic curve of the variation of the light absorption in glass and its semilogarithmic anamorphosis.

Fig. 6. Temperature dependence of the rate constants of the reducing process.

The kinetics of the diffusion-chemical processes in glasses has not been studied adequately, which pertains fully to $K_2O - PbO - SiO_2$ glasses. The results of investigations of the physical side of the reduction processes in lead – silica glass are reflected in [15, 16], but the kinetics of the diffusion-chemical interaction remains unknown.
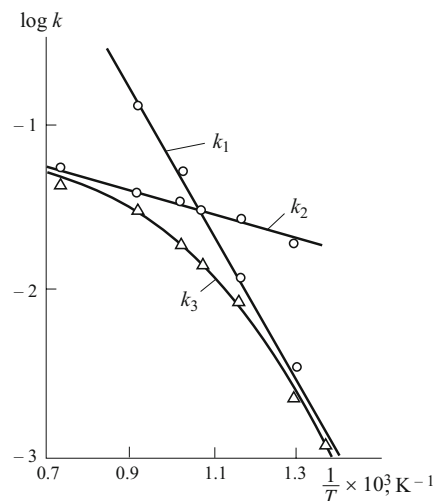
Experimental and commercial glasses were used to investigate gas-plasma heat-treatment processes. The glass samples were initially treated with a fixed reducing flame from burning natural gas with gas-reduced content 5.3%, including 2.2% H_2 and 3.1% CO.

The integral light absorption of a sample in the visible range of the spectrum, as determined with a spectrophotometer in the interval 400 – 800 nm with the light absorption varying in this region uniformly over the spectrum, was used as the characteristic of the reducing process.

The temperature and surface electric-conductivity were also measured in the course of the measurements. Here the kinetic principle of the process stopping at a definite moment was used, so that all measurements were performed at room temperature. As a result of the rapid increase of the viscosity in the surface layers of the glass on cooling the state reached at a definite moment of heat treatment is reliably fixed.

The data obtained were used to perform physical-chemical analysis of the process as a whole and its individual stages. The main dependences are presented in Figs. 5 and 6.

Figure 5 shows the kinetic variations of the light absorption of samples treated in a reducing regime at temperature 815°C of the surface layers. The arrow shows that inflection point of the curve. This point corresponds to the maximum of the surface electric conductivity. The electric conductivity increases from 1.6×10^{-15} to 2.04×10^{-9} S/m. The presence of an inflection point attests to the two-stage nature of the reducing process. At the first stage, as a result of a surface chemical reaction, reduction of lead occurs initially into an atomically disperse form [15, 16] followed by aggregation into nanoparticles. Lead atoms serve as centers facilitat-

ing electron exchange. The surface of the glass acquires properties of a semiconductor with a considerable fraction of electronic conductivity, which is noted by the maxima of the surface electric conductivity and the rate of growth of light absorption. Thus, a short-time change of the characteristics of the surface layer occurs. Aggregation of nanoparticles into larger formations (clusters) between which glass layers appear occurs at the second stage. The surface electric conductivity drops because of the loss of the electronic component. At the same time the reduced lead evaporates from the surface, reducing gases penetrate into the bulk of the glass, and lead is reduced in the lower-lying layers. However, the semiconducting state with electronic conductivity is reached only for the surface layer. The growth of light absorption slows down substantially; this is indicated by the course of the kinetic curve after the inflection point. At this stage of the reduction process the increase of the thickness of the reduced layer is combined with evaporation of lead from the surface layers. The slowing of the growth of light absorption is also related with diffusion difficulties for the reducing gases as they penetrate into the bulk of the glass.

The experimental data show that reduction is a diffusion-kinetic process, and at the first stage the process proceeds in the kinetic region. The separation of the kinetic curve into two sections and the semilogarithmic anamorphosis shows that each stage of the reducing process is a first-order process. The rate constants of each stage of the reduction processes are 0.138 and 0.027 sec^{-1}, respectively.

For the diffusion-kinetic regime, in conformance to [17], the total rate constant of reduction is given by

$$K = \frac{k_1 k_2}{k_1 + k_2}, \qquad (6)$$

where k_1 and k_2 are rate constants of the chemical reaction and diffusion process.

The relation (6) makes it possible to determine two limiting regions of the diffusion-kinetic process. For $k_1 \ll k_2$, $K \approx k_1$ the process proceeds in the kinetic region and its rate is completely determined by a kinetic chemical reaction. For $k_1 \gg k_2$, $K \approx k_2$ the process occurs in the diffusion region.
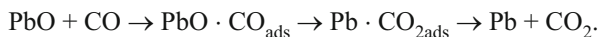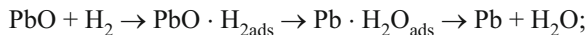
As noted above, the reduction process occurring on the surface can be regarded as proceeding in the kinetic region as a result of continuous access of reagents with constant concentration to the surface. The rate constant of the first stage is the rate constant of a chemical reaction: $k_1 = 0.138$ sec^{-1}. At the same time the process at the second stage proceeds in a diffusion-kinetic regime, and the rate constant determined is a total rate constant of the process: $K = 0.027$ sec^{-1}. The relation (6) gives $k_2 = 0.035$ sec^{-1}.

Comparing the values obtained for the rate constants shows that at a temperature of the surface layers 815°C in the interval 19 – 30 sec (at the second stage) the reduction process proceeds in the diffusion region.

The process passes into the kinetic region as temperature decreases. The determination of the kinetic characteristics of the process at different temperatures makes it possible to establish the temperature dependence of the rate of the process as a whole and in limiting regions. This dependence for the rate constants of the process in the different regimes is shown in Fig. 6, whence the temperature regions where the kinetic and diffusion regimes occur can be seen. The point of intersection of the straight lines corresponds to the temperature at which the rate constants of these regimes are the same. As temperature increases, the process shifts into the diffusion region and, vice versa, as it decreases, the process shifts into the kinetic region.

The mechanism of the reduction process can be explained from the adsorption standpoint. When the process occurs on the surface of glass, initially adsorption of the reducing gas on the reaction surface occurs on the reaction surface, and this is follows by detachment of oxygen from the lead complex and transfer of the oxygen to the adsorbed molecules of the reducing gas, which process is accompanied the appearance of the reducing phase of the metallic lead and, finally, desorption of the gaseous product formed.

The process of lead reduction on the surface can be represented in a general form as follows:

$$PbO + H_2 \rightarrow PbO \cdot H_{2ads} \rightarrow Pb \cdot H_2O_{ads} \rightarrow Pb + H_2O;$$

$$PbO + CO \rightarrow PbO \cdot CO_{ads} \rightarrow Pb \cdot CO_{2ads} \rightarrow Pb + CO_2.$$

The uniqueness of the structure function of lead in the glasses, which is connected with the high polarizability an electronic shell, results in the formation of definite structurally formed lead-oxygen groups [11] with comparatively low force characteristics. The binding energy in these groups equals 75 – 163 kJ/mole, while in H_2 and CO — 433 and 945 kJ/mole [14]. Thus the particles are much more mobile in lead-oxygen groups, facilitating breaking of the bonds in them. At the same time the asymmetry of these groups,

which is associated with the different magnitude of the Pb – O binding energy, corresponds to the deformation of adsorbed molecules of the reducing gases with weakening or rupturing of the bonds. As a result, favorable conditions are created for the formation of H_2O and CO_2 molecules. The donor form of the chemisorption of reducing gases increases the concentration of free electron, which are expended on the reduction of lead in an atomically dispersed form followed by the formation of nanoparticles ($Pb^{2+} + 2e \rightarrow Pb$) and facilitate the appearance of an electronic component in the surface layer. The activation energy of the reduction reaction, determined from the kinetic data ($E_a = 86$ kJ/mole), has turned out to be comparable to the Pb – O binding energy, showing that the rate of rupture of these bonds determines the rate of the rate of a chemical act of reduction. When the reduction process is complete, aggregation of nanoparticles of metallic lead with formation of clusters occurs and the distances between the enlarge particles increase. Under these conditions electron exchange becomes impossible, and the electric conductivity decreases as a result of the loss of the electronic component.

The volatilization of metallic lead from the surface of a layer results in the formation of a microlayer of glass which does not contain reduced lead. The reduction process in the low-lying layers occurs with the diffusion of reducing gases through the surface layers of the glass. As a result of the micro-heterogeneity of lead-containing glasses, the reducing gases penetrate into the glass along the boundaries of the nonuniformities; the reducing processes proceed nonuniformly with local limitations. A transition of electrons from neighboring anions of the lead-oxygen groups in glass is possible on the glass – metal interface which arises. The disrupted electroneutrality of a microsection gives rise to migration of electrons toward surface and facilitates binding of the reducing gases with oxygen. On the other hand, having gained negative charge the metal attracts the cations Pb^{2+} from the lead-oxygen groups. Breaking existing bonds with oxygen, the cations collectively incorporate the general electron cloud of the metal and become its main part. The metallic lead particles grow. Because the process develops nonuniformly, interlayers of glass are present between the particles of reduced lead, and a state with electron-ion conductivity does not arise.

The oxidation of the reduced layer of metallic lead occurs by means of the action of an oxidative flame on the sample. The oxidation of metallic lead consists of oxygen diffusion toward the lead – glass interface, adsorption of oxygen on this boundary, and formation of lead-oxygen complexes. In contrast to the reducing gases, oxygen is adsorbed as an electron acceptor:

$$O_{2(gas)} \rightarrow 2O_{(ads)} + 2e \rightarrow 2O^-.$$

Metallic lead serves as a source of electrons:

$$Pb \rightarrow Pb^{2+} + 2e.$$

This creates conditions for the formation of lead-oxygen complexes which enter into the structure of the glass. The sizes of the particles of metallic lead decrease until the particles vanish completely.

Gas-plasma heat-treatment of lead-containing glass is used for soldering the constituent parts of electro-vacuum and illumination-technological articles, in the production of home glassware with heat-treatment of the surface and edges of crystal articles [4, 6, 18]. "Soft" (reduced) and "hard" (oxidized) flames of the burners are used.

In fire polishing the edges of articles made of lead crystal, a two-stage heat-treatment technology was developed. At the first stage the edge of an article is exposed to a "soft" flame. In so doing, first, the lead on the surface is reduced and volatilizes and a microlayer of lead-free glass is formed. Next, the reduction of lead proceeds beneath the surface layer with reducing gases diffusing through it. The reduced-glass layer formed in the process screens heat from reaching the lower-lying layers and leads to soft heating and partial melting of the edge. At the second and final stage of the process, under the action of the "hard" flame, oxygen diffuses through the thin surface layer and oxidizes the particles of reduced lead.

The technology has been tests and adopted at the Gus'-Khrustal'nyi works. Acceleration of the melting process is observed, the appearance of rejects due to deformation of the edge and separation of a ring-shaped strip at the top edge of the article, and other phenomena are observed.

The generalized kinetic analysis of the processes in glasses in the system K$_2$O – PbO – SiO$_2$ has made it possible to obtain data reflecting the role of surface and volume factors accompanying heterogeneous interaction, including a stage of formation of nanoparticles, as is indicated by the short-time change of the characteristics of the surface layer. Further development of this direction is necessary in connection with the development of nanotechnologies, in which surface phenomena play a determining role.

REFERENCES

1. G. A. Lykova, *Structure and Properties of Inorganic Glasses: Index of Scientific and Technical Literature* [in Russian], BAN, Leningrad (1986).
2. O. V. Mazurin, M. V. Strel'tsina, and T. P. Shvaiko-Shvaikovskaya, *Handbook of the Properties of Glasses and Glass-Forming Melts* [in Russian], Nauka, Leningrad (1977), Vol. 3.
3. L. I. Demkina (ed.), *Physico-Chemical Principles of the Production of Optical Glass* [in Russian], Khimiya, Leningrad (1976).
4. Yu. A. Guloyan, *Technology of Glass and Glass Articles* [in Russian], Transit-Iks, Vladimir (2003).
5. S. Bach, F. Baukke, R. Brükner, et al., *Forms of Rejects in the Production of Glass*, edited by H. Jebsen-Marvedel and R. Brükner [Russian translation], Stroiizdat, Moscow (1986).
6. N. I. Churkina, V. V. Lityushkin, and A. P. Sivko, *Principles of the Technology of Electric sources of Light*, MKI, Saransk (2003).
7. J. Matousek, "Volatilization of lead glasses within the 1200 to 1400 temperature range," *Silikaty*, **16**(1), 1 – 9 (1972).
8. M. Cable, C. Arak, and M. Chaundry, "The kinetics of volatilization from lead glasses," *Glastecnische Berichte*, **48**(1), 1 – 6 (1975).
9. Yu. A. Guloyan, "Investigation of the kinetics of heterogeneous chemical interaction with the formation of glass melt in the system Na$_2$O – SiO$_2$," *Zh. Prikl. Khim.*, **52**(9), 1967 – 1971 (1979).
10. N. M. Émmanuél' and D. G. Knorre, *Course in Chemical Kinetics* [in Russian], Vyssh. Shk., Moscow (1969).
11. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1974).
12. O. A. Esin and P. V. Gel'd, *Physical Chemistry of Pyrometallurgical Processes* [in Russian], Metallurgiya, Moscow (1966), Pt. 2.
13. M. Jaycock and J. Parfit, *Chemistry of Interphase Surfaces* [Russian translation], Mir, Moscow (1984).
14. T. Cottrell, *Strength of Chemical Bonds* [Russial translation], Mir, Moscow (1956).
15. K. Blodgett, *Strength of Chemical Bonds* [Russian translation], Inostr. Lit., Moscow (1956).
16. V. I. Shelyubskii, *Investigation of the Process of Reduction of Lead during Heat Lead Glass in a Reducing Flame, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1955).
17. D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics* [in Russian], Nauka, Moscow (1987).
18. Ya. Shpachek and K. Peshek, *Manual Extraction of High-Grade Dishware and Consumer Artisan Glass* [in Russian], Legkaya industriya, Moscow (1974).